

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>H05B 33/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/03565</b> <b>(43) International Publication Date:</b> 20 January 2000 (20.01.00)
<b>(21) International Application Number:</b> PCT/US99/15437 <b>(22) International Filing Date:</b> 9 July 1999 (09.07.99) <b>(30) Priority Data:</b> 60/092,418 10 July 1998 (10.07.98) US <b>(71) Applicant:</b> FED CORPORATION [US/US]; Hudson Valley Research Park, 1580 Route 52, Hopewell Junction, NY 12533 (US). <b>(72) Inventor:</b> OLDHAM, Warren, Jr.; 10 B Chelsea Ridge Drive, Wappingers Falls, NY 12590 (US). <b>(74) Agent:</b> COYNE, Patrick, J.; Collier, Shannon, Rill & Scott, PLLC, Suite 400, 3050 K Street, N.W., Washington, DC 20007 (US).		<b>(81) Designated States:</b> European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> AMORPHOUS MOLECULAR MATERIALS FOR OPTOELECTRONIC DEVICES AND PROCESS FOR PRODUCING THE SAME  <b>(57) Abstract</b>  The present invention comprises an organic light emitting device comprising a first electrode, a second electrode, and an organic stack interposed between the first electrode and the second electrode, wherein the organic stack further comprises at least one organic layer, wherein the organic layer further comprises organic compounds such that the organic light emitting device continues to function in temperatures in excess of 145 °C. The organic layer may be comprised of organic compounds with tetrahedral shaped core structures, tetrahedral shaped core structures containing aromatic side groups, tetrahedral shaped core structures containing aromatic amine side groups, symmetrical tetrahedral shaped core structures, symmetrical tetrahedral shaped core structures containing aromatic side groups, and/or symmetrical tetrahedral shaped core structures containing aromatic amine side groups.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## **AMORPHOUS MOLECULAR MATERIALS FOR OPTOELECTRONIC DEVICES AND PROCESS FOR PRODUCING THE SAME**

### **Cross Reference To Related Patent Application**

This application relates to and claims priority on United States Provisional Application Serial No. 06/092,418, entitled "AMORPHOUS MOLECULAR MATERIALS FOR OPTOELECTRONIC DEVICES AND PROCESS FOR PRODUCING THE SAME", filed July 10, 1998.

### **Field of the Invention**

The present invention relates generally to compounds for use in organic light emitting devices (OLEDs). More particularly, the present invention relates to novel highly symmetrical tetrahedral shaped aromatic and/or aromatic amine containing molecules, and their syntheses, for application in high temperature OLED displays.

### **Background of the Invention**

Careful analysis of the thermal behavior of organic light emitting devices (OLED) indicates morphological instability of the hole transport layer as the limiting element of thermal stability. Before considering this point in detail, Applicant first describes film morphology in general and how it relates to device performance. The organic materials useful in OLED applications are intrinsic insulators and require large electric fields to conduct charge. This requirement is made practical because the thickness of the complete organic stack of organic layers is only some 1500 Å, enabling a drive voltage of less than 6 volts to product light output at typical television brightness levels. The morphology of the organic layers in the organic stack controls charge mobility through the device, which in turn is a key factor in efficiency. Although charge transport in perfect, defect-free single crystals is considered most efficient compared to

**SUBSTITUTE SHEET (RULE 26)**

other morphologies (polycrystalline or amorphous). it has not proven practical to obtain monocrystalline ultra-thin films over large areas. Polycrystalline films, composed of many closely associated and interpenetrating microcrystals, always contain a high density of grain boundaries, which cause serious structural defects and deep carrier traps. Instead, completely amorphous molecular films provide a good compromise in performance. Amorphous films allow uniform charge injection across the entire electrode surface, whereas polycrystalline films are plagued by local hot spots of high current density that ultimately lead to device instability. Similarly, charge mobility and electroluminescence quantum efficiency also depends on film morphology. Campbell and co-workers have shown that chemically identical materials, prepared either as amorphous or as polycrystalline films, show significantly different OLED performance. (Joswick, M.D.; Campbell, I.H.; Brashkov, N.N.; Ferraris, J.P. *J. Appl. Phys.* 1996, 80, 2883-2890). While the photoluminescence properties of the different films were very similar, it was found that charge mobility and electroluminescence quantum yield were more than an order of magnitude greater in the amorphous samples. Furthermore, according to Forrest the "amorphous structure leads to a high radiative recombination efficiency of Frenkel excitons due to a reduction in quenching from internal conversion processes linked to highly coupled, crystalline organic systems." (Forrest, S.R. *Chem. Rev.* 1997 97, 1793-1896.)

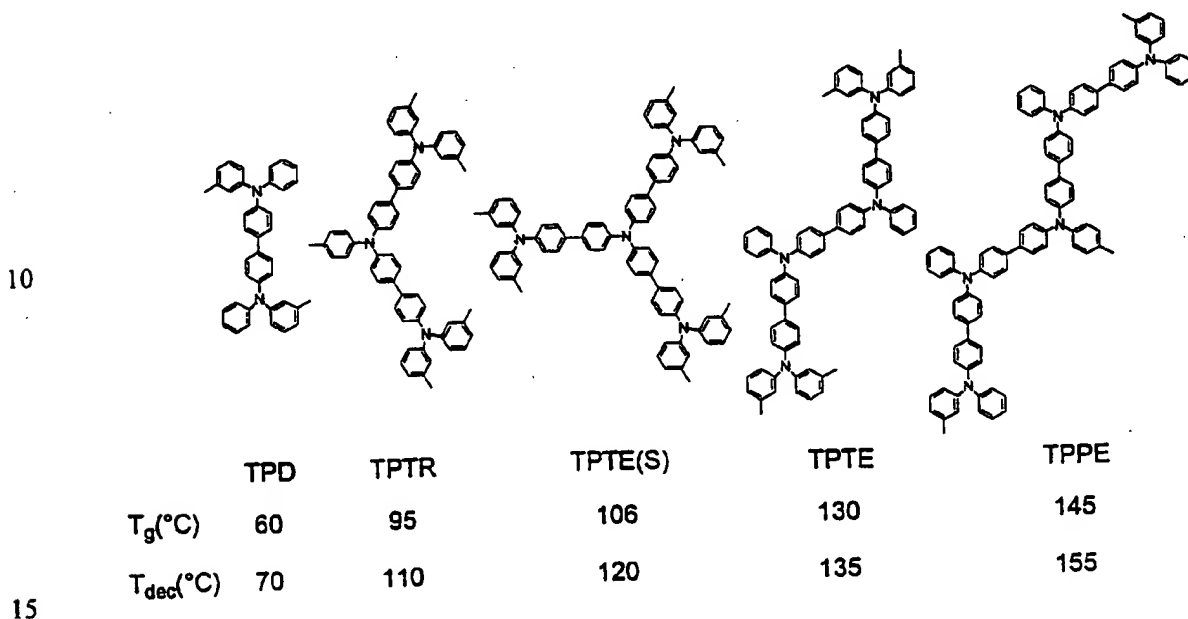
Amorphous molecular films are easily fabricated using the thermal deposition method. Variables such as deposition rate and temperature of substrate can be tuned to control film morphology. As a rule, higher deposition rates and cooler substrate temperatures each favor the preparation of amorphous molecular films. Once formed however, most molecular films tend to crystallize at room temperature because the amorphous morphology is generally a non-equilibrium phase, higher in energy than the ordered crystalline (polycrystalline) phase. The rate of film crystallization depends on the ambient temperature and its relation to the glass transition temperature ( $T_g$ ) of the material. A second important factor controlling film crystallization is

maximum crystallization velocity (MCV), which is also characteristic of a particular material. Stable amorphous films will have a high  $T_g$  and a low MCV. If the  $T_g$  value of an amorphous material is greater than its thermal environment, that material will tend to remain amorphous. Similarly, if the MCV is very low, even at high temperatures some materials will remain amorphous indefinitely. It is possible to relate these thermodynamic and kinetic factors to understand how molecular design can be optimized to yield thermally stable amorphous molecular films. From this analysis, Naito has concluded that thermally stable organic dye glasses can be formed from large, symmetric, globular, rigid, and dense molecules. ((a) Naito, K.; Miura, A. *J. Phys. Chem.* 1993 97, 6240-6248. (b) Naito, K. *Chem. Mater.* 1994 6, 2343-2350.) Thin-film materials developed by Kodak have unusually good thermal stability because some of these design criteria have been satisfied. However, recent discoveries of even higher  $T_g$  materials indicate that molecular materials stable up to 175°C is a realistic goal in the short term. An object of the present invention is to obtain very high  $T_g$  materials that remain amorphous even above the glass transition temperature.

#### 15 Thermal Instability of Hole Transport Layer

In multilayer OLEDs, it can be shown that the onset temperature of rapid device degradation is correlated with the  $T_g$  of the hole conducting layer. Of the materials used to fabricate OLEDs, the hole transport materials currently have the lowest  $T_g$  values. For example,  $T_g$  of NPB is 95°C compared to 175°C for the electron transport material, Alq<sub>3</sub>. An informative report by Tokito, et al. highlights the limiting thermal stability of the hole-conducting layer. ((a) Tokito, S.; Tanaka, H.; Okada, A.; Taga, Y. *Appl. Phys. Lett.* 1996, 69, 878-880. (b) Tokito, S.; Tanaka, H.; Noda, K.; Okada, A.; Taga, Y. *Appl. Phys. Lett.* 1997, 70, 1929-1931.) In this work a series of five different oligomeric triphenylamines were prepared having  $T_g$  values ranging from 60 to 145°C. Simple OLED devices were constructed using the various triphenylamine compounds as the hole conduction layer and Alq<sub>3</sub> as the emitting layer. The experiment was

carried out by driving each device at a constant current of 11 mA/cm<sup>2</sup> and gradually increasing the ambient temperature from room temperature upwards. For each device, a dramatic drop in electroluminescence output was observed just above the  $T_g$  of each hole conducting layer. Shown below are the five hole conducting compounds with their  $T_g$  values and the temperature at which electroluminescence output rapidly degraded.



The thermal mechanism that causes light output to rapidly degrade just above  $T_g$  is generally ascribed to crystallization of the hole transport layer. (Han, E.; Do, L.; Niidome, Y.; Fujihira, M. *Chem. Lett.* 1994, 969-972.) More recently, Fenter et al. have argued, based on X-ray specular reflectivity measurements (Fenter, P.; Schreiber, F.; Bulovic, V.; Forrest, S.R. *Chem. Phys. Lett.* 1997, 277, 521-526.) that film interfaces between the hole conducting material and Alq<sub>3</sub> are damaged because the hole conducting material undergoes a large thermal expansion at the glass transition temperature. However, for either damage mechanism (crystallization or thermal expansion), it seems clear that the greatest thermal stability benefit, combined with the least technical risk, can be accomplished by increasing the  $T_g$  of the hole transport layer. If crystallization is truly the cause of device failure, this thermal degradation mechanism can be

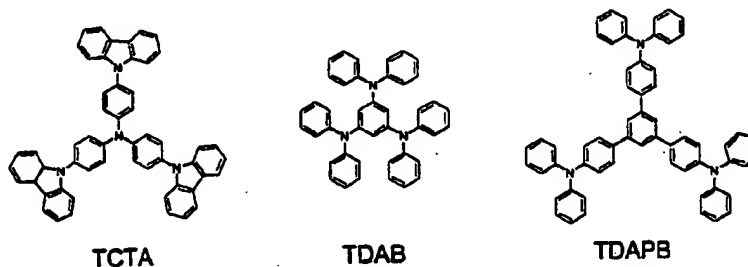
20

25

eliminated because molecular materials can be designed with very low crystallization velocities that will remain amorphous even above  $T_g$ .

### Technical Solution to Achieve Thermally Stable Hole Transport Materials

In general, tertiary aromatic amines have been found to function very well as hole conducting materials due to a low ionization potential and good hole mobility. However, the most simple aromatic amines, such as triphenylamine, do not form stable amorphous films. Assembling larger molecules such as in the case of the benzidine compounds (e.g. NPB) can be used to improve the film forming properties. The synthetic strategy that has been followed to further increase glass transition temperatures of these materials links aromatic amines together to form either "starburst" structures (shown below). (See for example: (a) Shirota, Y.; Kobata, T.; Noma, N. *Chem. Lett.* 1989, 1145-1148. (b) Ishikawa, W.; Inada, H.; Nakano, Y.; Shirota, Y. *Chem. Lett.* 1991, 1731-1734. (c) Inada, H.; Shirota, Y., *J. Mater. Chem.* 1993, 3, 219-320. (d) Kuwabara, Y.; Ogawa, H.; Inada, H.; Noma, N.; Shirota, Y. *Adv. Mater.* 1994, 6, 677. (e) Kageyama, H.; Itano, K.; Ishikawa, W.; Shirota, Y. *J. Mater. Chem.* 1996, 6, 675-676.) or linear oligomers (shown in previous figure, above), (Tanaka, H.; Tokito, S.; Taga, Y.; Okada, A. *J. Chem. Soc., Chem. Commun.* 1996, 2175-2176.) For the "starburst" structures the central core has been either triphenylamine or 1,3,5-substituted benzene.



The practical limit of the linear oligomer structures is probably the pentamer labeled as TPPE, above. Higher molecular weight molecules become increasingly more difficult to sublime without heating above chemical decomposition temperatures. The open linear structure allows adjacent molecules to interact over a large portion of their molecular surface and would be

expected to have the greatest difficulty in thermal sublimation. Thermal sublimation requires that the weak intermolecular forces holding the molecules in the solid state must be broken to force the molecules in the gas phase. In contrast, perfectly symmetrical spherical structures should only interact with adjacent molecules at their periphery. In principle, much larger  
5 molecular weight materials should be accessible without drastically compromising the compound's volatility. The known "starburst" structures have not utilized central cores that enforce truly spherical geometry. The 1,3,5-substituted benzene ring is trigonal planar and triphenylamine is trigonal pyramidal.

10

### Objects of the Invention

It is therefore an object of the present invention to create novel compounds for use in OLEDs.

It is yet another object of the present invention to design and synthesize novel compounds with an increased glass transition temperature ( $T_g$ ) for use in OLEDs.

15

It is a further object of the present invention to design and synthesize novel compounds that have a decreased maximum crystallization velocity for use in OLEDs.

It is still another object of the present invention to design and synthesize novel compounds which will result in an OLED with an increased brightness.

20

It is yet another object of the present invention to design and synthesize novel compounds which will provide OLEDs with an increased lifetime.

It is still yet another object of the present invention to design and synthesize novel compounds which will resist crystallization and high temperatures for use in OLEDs.

It is still yet another object of the present invention to design and synthesize molecules with tetrahedral structures for use in OLEDs.



It is still yet another object of the present invention to design and synthesize compounds which have a symmetrical tertiary structure for use in OLEDs.

It is still yet another object of the present invention to design and synthesize large symmetrical molecules that can be sublimed for use in OLEDs.

5 It is still yet another object of the present invention to design and synthesize novel compounds that will not quench one another when used in OLEDs.

It is still yet another object of the present invention to design and synthesize molecules with a tetrahedral core containing poly-ring structures for use in OLEDs.

10 It is still yet another object of the present invention to use molecular design to control the morphology of molecules used in OLEDs.

It is still yet another object of the present invention to design and synthesize novel symmetrical tetrahedral compounds with good film forming properties for use in OLEDs.

15 Additional objects and advantages of the invention are set forth, in part, in the description which follows and, in part, will be apparent to one of ordinary skill in the art from the description and/or from the practice of the invention.

20 It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only, and are not restrictive of the invention as claimed. The accompanying drawings, which are incorporated herein by reference, and which constitute a part of this specification, illustrate certain embodiments of the invention, and together with the detailed description serve to explain the principles of the present invention.

### Summary of the Invention

In response to the foregoing challenges, Applicant has developed innovative organic compounds for use in an organic light emitting device. The organic compounds contain

tetrahedral shaped core structures allowing the organic light emitting device to operate at increased temperatures.

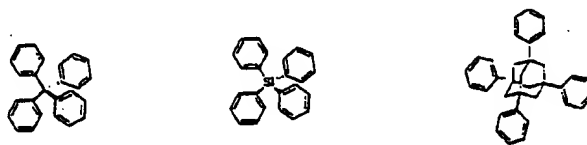
The present invention comprises an organic light emitting device comprising a first electrode, a second electrode, and an organic stack interposed between the first electrode and the second electrode, wherein the organic stack further comprises at least one organic layer, wherein  
5 the organic layer further comprises organic compounds such that the organic light emitting device continues to function in temperatures in excess of 145° C.

The organic layer may be comprised of organic compounds with tetrahedral shaped core structures, tetrahedral shaped core structures containing aromatic side groups, tetrahedral shaped  
10 core structures containing aromatic amine side groups, symmetrical tetrahedral shaped core structures, symmetrical tetrahedral shaped core structures containing aromatic side groups, and/or symmetrical tetrahedral shaped core structures containing aromatic amine side groups.

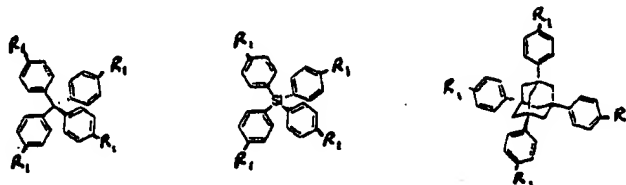
The aromatic side groups may be, but are not limited to, phenyl, naphthyl, anthracyl, carbazole, and any and all substituted analogs thereof. The tetrahedral or symmetrical tetrahedral  
15 shaped core structure may be a tetraphenyl compound, including, but not limited to, tetraphenylmethane, tetraphenylsilane, tetraphenyladamantane, tetraphenylgermane, tetraphenylplumbane, and/or tetramethylstannane. The tetraphenyl compound may be functionalized at the *para*-position.

The tetrahedral shaped core structures may satisfy one or more of the formula  $(C_6H_5)_4R$ ,  
20 where R may be, but is not limited to, C, Si, adamantane ( $C_{10}H_{12}$ ), Ge, Pb, or Sn. The organic compounds with tetrahedral shaped core structures may satisfy one or more of the formula  $R_1(C_6H_5)_3R$ , where  $R_1$  may be, but is not limited to, aromatic groups and/or aromatic amine groups, and where R may be, but is not limited to, C, Si, adamantane ( $C_{10}H_{12}$ ), Ge, Pb, or Sn.

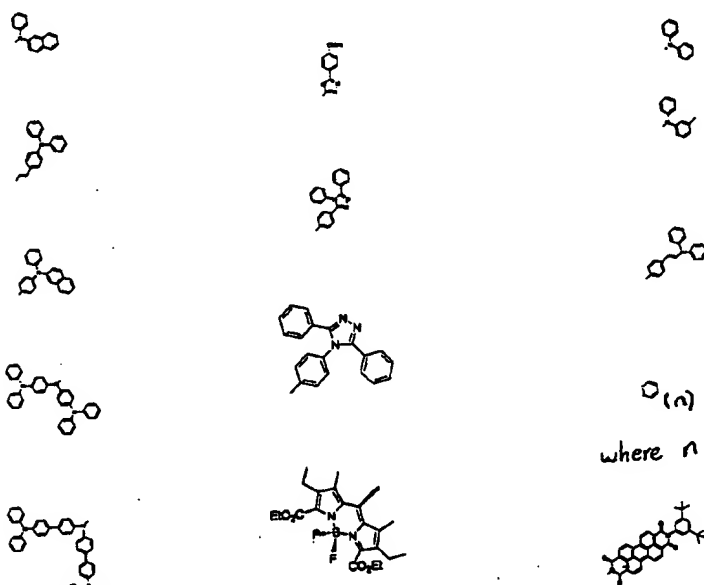
The tetrahedral shaped core structures may be, but are not limited to:



5 The organic layer may contain, but is not limited to, organic compounds selected from the group consisting of:



10 where  $R_1$  may be, but is not limited to, the group consisting of:

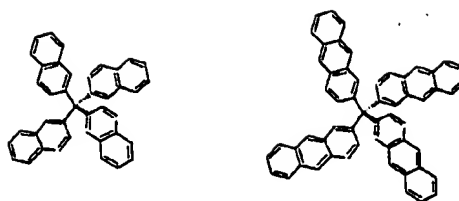


20

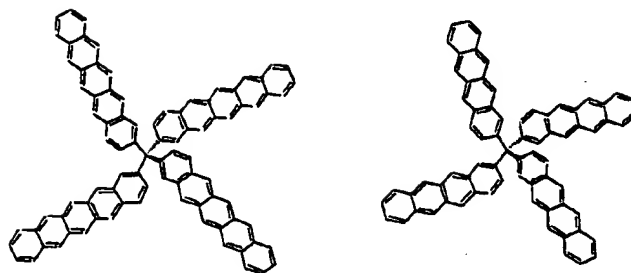
The organic compounds with a tetraphenyl core may be, but are not limited to, the group consisting of:

25

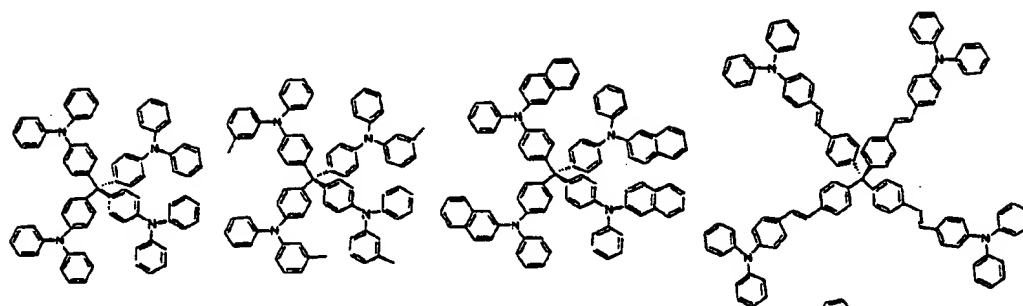
5



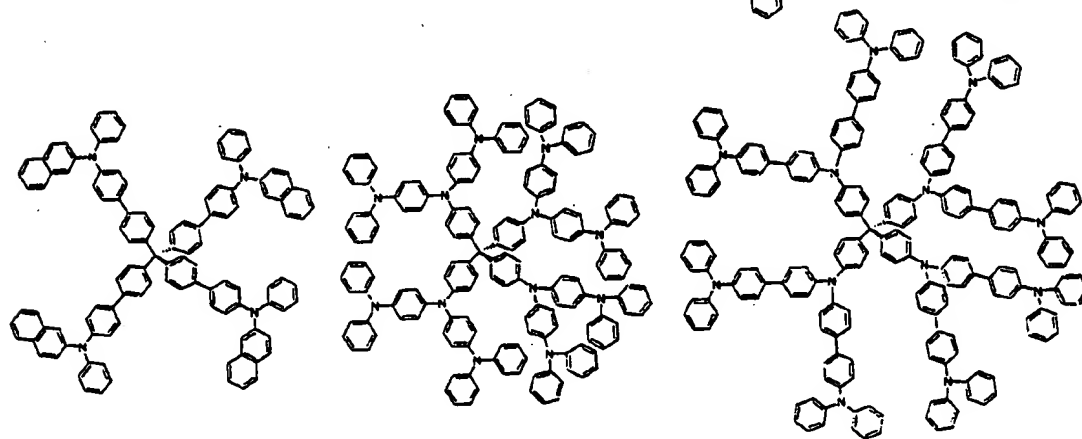
10



15



20



25

10

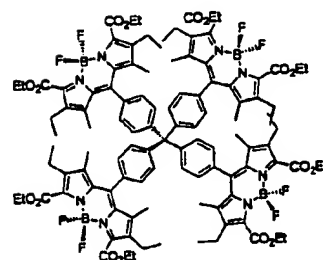
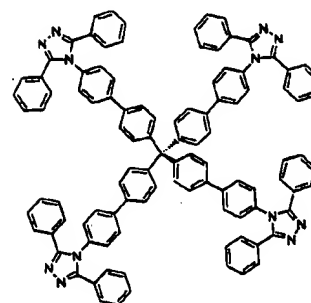
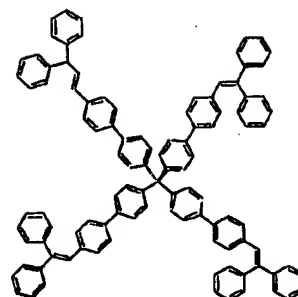
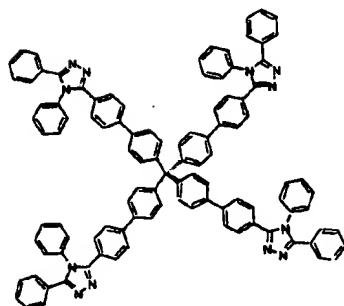
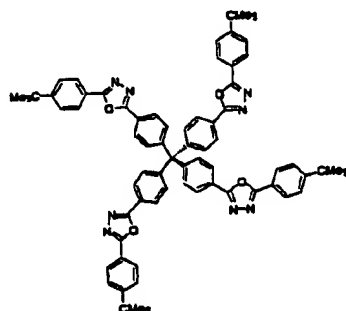
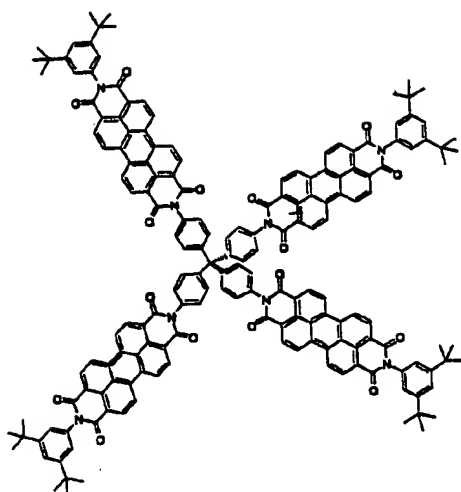
5

10

15

20

25



The tetraphenyl core may be, but is not limited to, tetraphenylmethane, tetraphenylsilane, tetraphenyladamantane, tetraphenylgermane, tetraphenylplumbane, and/or tetramethylstannane.

The present invention comprises an organic light emitting device having a first electrode, a second electrode, and an organic stack interposed between the first electrode and the second electrode, where the organic stack may further comprise at least one hole transport layer. The hole transport layer may further comprise organic compounds with tetrahedral shaped core structures.

The organic compounds of the at least one hole transport layer may be comprised of tetrahedral shaped core structures, tetrahedral shaped core structures containing aromatic side groups, tetrahedral shaped core structures containing aromatic amine side groups, symmetrical tetrahedral shaped core structures, symmetrical tetrahedral shaped core structures containing aromatic side groups, and/or symmetrical tetrahedral shaped core structures containing aromatic amine side groups.

The aromatic side groups may be, but are not limited to, phenyl, naphthyl, anthracyl, carbazole, and any and all substituted analogs thereof. The tetrahedral or symmetrical tetrahedral shaped core structure may be a tetraphenyl compound, including, but not limited to, tetraphenylmethane, tetraphenylsilane, tetraphenyladamantane, tetraphenylgermane, tetraphenylplumbane, and/or tetramethylstannane. The tetraphenyl compound may be functionalized at the *para*-position.

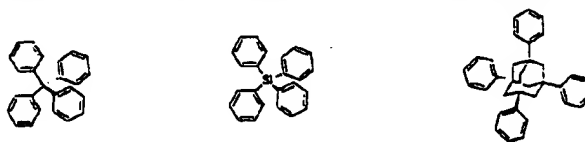
The organic layer of the present invention may further comprise organic compounds containing tetrahedral shaped core structures including, but not limited to, silicon based tetrahedral core structures, carbon based tetrahedral core structures, adamantane based tetrahedral core structures, germane based tetrahedral core structures, plumbane based tetrahedral core structures, and stannane based tetrahedral core structures. In addition, the tetrahedral shaped core

structures may contain aromatic side groups and/or aromatic amine side groups oriented away from one another at angles between 100° and 120°.

## Detailed Description of the Invention

5           Reference will now be made in detail to a preferred embodiment of the present invention. The present invention describes novel highly symmetrical tetrahedral shaped aromatic amine containing molecules and their syntheses for application as hole conduction materials in high temperature OLED displays. Applicant has identified tetraphenylmethane, tetraphenylsilane and tetraphenyladamantane as very attractive candidates to serve as rigid tetrahedral core structures.

10



Tetraphenylmethane   Tetraphenylsilane   Tetraphenyladamantane

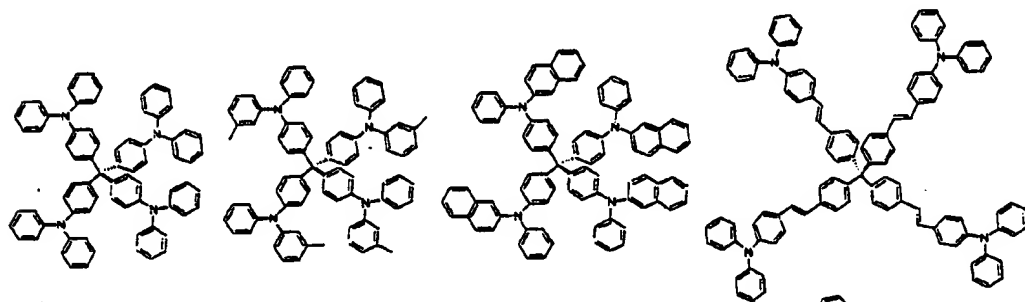
The tetrahedral core structures shown above are easily obtained in large quantities using developed synthetic methodology. ((a) Wilson, L.M.; Griffin, A.C. *J. Mater. Chem.* 1993, 3, 991-994. (b) Su, D.; Menger, F.M. *Tetrahedron Lett.* 1997, 38, 1485-1487. (c) Liu, F.-Q.; Tilley, T.D. 1997, 36, 5090-5096. (d) Mathias, L.J.; Reichert, V.R.; Muir, A.V.G. *Chem. Mater.* 1993, 5, 4-5.) They can be selectively functionalized at the *para*-position of the phenyl groups to allow a wide variety of organic units to be assembled around the tetrahedral core. The central  $sp^3$ -hybridized carbon or silicon atom, or the adamantane group electronically isolates each arm of the tetrahedron from one another. Applicant expects some variation in this characteristic, where the degree of electronic communication is ordered  $Si > C \gg$  adamantane. This variation can be used to effectively tune the electronic properties of the new materials. The rigid tetrahedral framework orients the appended groups away from one another at an angle of between 100° and 120°, or approximately 109.5°, and reduces the possibility of forming intramolecular

20

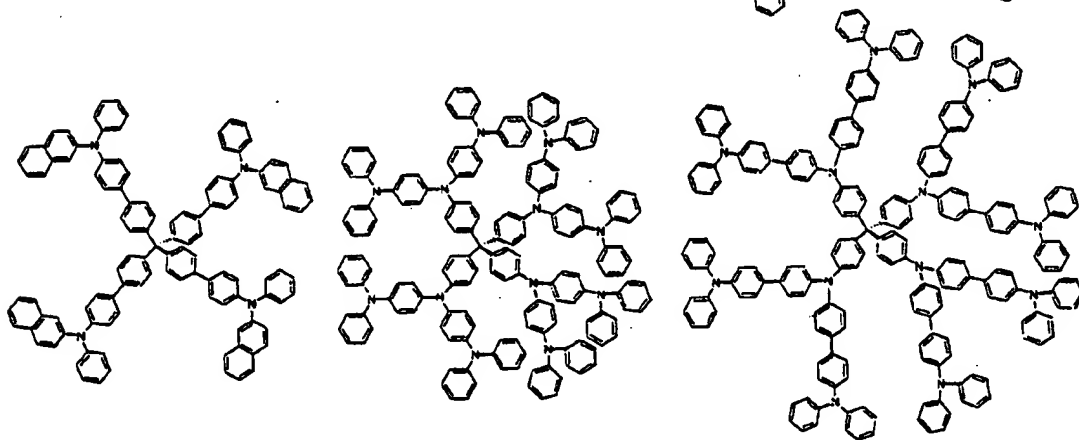
$\pi$ -stacked compounds. If rigid dye molecules are coupled in the tetrahedral array, the proposed molecular design should discourage undesirable intramolecular aggregate or exciplex formation. Also because the organic dye molecules radiate from a central tetrahedral core, they are hindered from forming intermolecular  $\pi$ -aggregates in solid state films, thereby preventing luminescence quenching effects.

Aside from the molecular design advancements of tetrahedral-shaped molecules, improvements in synthetic strategy allow these materials to be prepared in significantly higher yield compared to the classical Ullmann coupling reaction commonly used to prepare tertiary aromatic amines. Some examples of the types of molecules Applicant has pursued are shown below. For simplicity, the molecules depicted incorporate the tetraphenylmethane core, however related materials are also accessible using tetramethylsilane and tetraphenyladamantane.

15



20

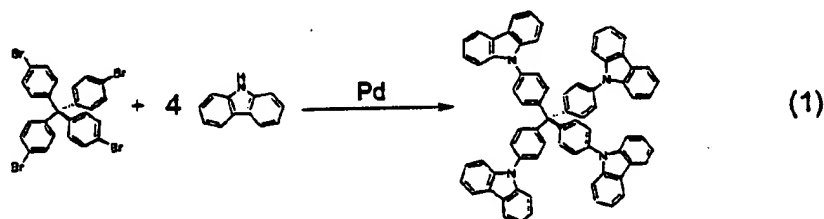




## Example 1

Our synthetic strategy to prepare these materials permits four aromatic and/or aromatic amine units to be coupled with the tetrahedral core in one reaction step. This so-called convergent approach allows high molecular weight materials to be obtained quickly and cleanly. As an example, the reaction of carbazole and *tetrakis*(4-bromophenyl) methane is shown in eq.

1.



10

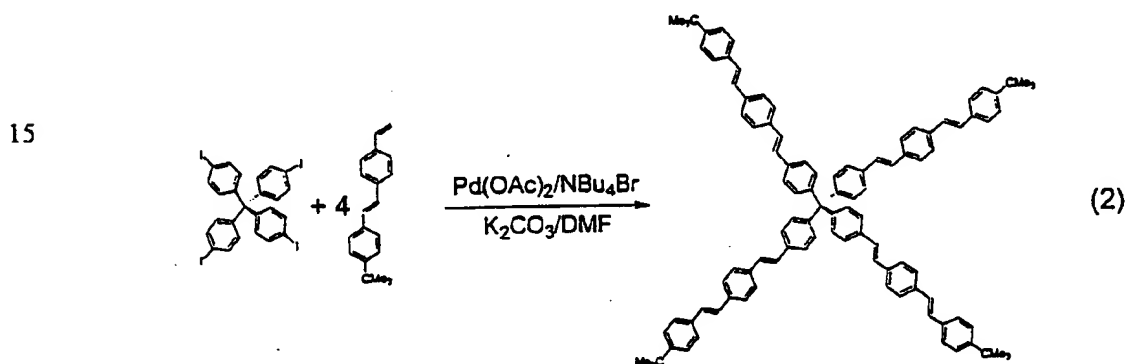
The palladium catalyzed phenyl-amine coupling reaction is recently developed ((a) Hartwig, J.F. *Synlett* 1997, 4, 329-340. (b) Louie, J.; Driver, M.S.; Hamann, B.C.; Hartwig, J.F. *J. Org. Chem.* 1997, 62, 1268-1273. (c) Driver, M.S.; Hartwig, J.F. *J. Am. Chem. Soc.* 1996, 118, 7217-7218.) ((a) Marcoux, J.F.; Waagaw, S.; Buchwald, S.L. *J. Org. Chem.* 1997, 62, 1568-1569. (b) Wolfe, J.P.; Wagaw, S.; Buchwald, S.L. *J. Am. Chem. Soc.* 1996, 118, 7215-7216.) and has been utilized to prepare hole conducting type materials in high yield. ((a) Louie, J.; Hartwig, J.F.; Fry, A.J. *J. Am. Chem. Soc.* 1997, 119, 11695-11696. (b) Thayumanavan, S.; Barlow, S.; Marder, S.R. *Chem. Mater.* 1997, 9, 3231-3235.) For example, the palladium catalyzed method was used to prepare 4,4'4''-tris(N,N-diphenylamino)triphenylamine in 84% yield compared to only 22% using the Ullmann coupling reaction. Applicant has also pursued the synthesis of tetrahedral amine-containing materials that are linked to the core via phenyl-phenyl or phenyl-vinyl connections to further explore the effect of structural diversity on solid state morphology and thermal stability. The present invention allows a novel entry of a large number of different aromatic amines for use in OLEDs. The variety of aromatic groups such as phenyl and substituted analogs thereof, naphthyl, anthracyl, carbazolyl, etc. provides access to

25

range of possible structures. The approach of the present invention can be used to quickly screen many potential and novel hole transport materials, that will be selected for application based on hole transport properties and  $T_g$ . The novel materials should maintain the desirable hole transport properties common to aromatic amines, but will significantly extend the required high temperature morphological stability.

## Example 2

A quantitative measure of the improvements in  $T_g$  values anticipated for the proposed and novel aromatic amine containing materials may be roughly estimated from related tetrahedral stilbenoid compounds prepared by Oldham, et al. (Oldham, W.J., Jr.; Lachicotte, R.J.; Bazan, G.C. *J. Am. Chem. Soc.* 1998, 120, (in press). In this work, high  $T_g$  blue luminescent materials were prepared by coupling vinylstilbene derivatives to a tetraphenylmethane core using the palladium catalyzed Heck reaction (eq. 2).



20 The  $T_g$  value of the resulting *tetrakis(4-tert-butylstyryl)stilbene* was found to be 175°C by DSC analysis. No evidence for crystallization was observed even when heating samples to 350°C. Furthermore, powder X-ray diffraction measurements confirmed the completely amorphous morphology. Applicant concludes from this data that the tetrahedral core strategy provides materials with high  $T_g$  and very low crystallization velocities. Materials of this

25 class can be fabricated as amorphous thin-films that are completely stable against crystallization,

even when heated above their glass transition temperature. A significant advantage of the tetrahedral core molecular design over polymeric OLED materials is that it combines the traditional advantages of small molecules (e.g. high chemical purity and volatility) with those of polymers (e.g., high  $T_g$ , low MCV, thermal stability).

5           The hole transport materials proposed in this work are new compounds. An object of the present invention is to successfully prepare and purify the compounds for electronic applications. Although the proposed synthetic methods are developed and have been used successfully in related systems, the compounds of the present invention have not previously been synthesized. Another object of the present invention is to design and synthesize novel high molecular weight  
10           materials (expected to have the highest thermal stability), while retaining the volatility necessary to allow films to be fabricated by thermal sublimation. Applicant believes that the new materials containing four amine groups should possess the necessary volatility. The chemical stability of radical cations (also called holes) incorporating the core structures is unknown. Triphenylmethyl cation or triphenylmethyl radical are relatively stable species and the danger of disproportionation  
15           reactions upon injection of holes is a primary consideration. To mitigate against this possibility Applicant have also explored the use of the tetraphenyladamantane core which Applicant considers stable against disproportionation reactions. Finally, in another object of the present invention, the ionization potential of the new materials could be altered relative to NPB. If the ionization potential is reduced too much, then undesirable exciplex formation can occur at the  
20           interface of the hole transport layer and  $Alq_3$ . (Itano, K.; Ogawa, H.; Shirota, Y. *Appl. Phys. Lett.* 1998, 72, 636-638.) As such, another object of the present invention is to control the ionization potential to ameliorate this risk by judicious choice of aromatic groups bonded to nitrogen.

          It will be apparent to those skilled in the art that various modifications and variations can be made in the construction, configuration, and/or operation of the present  
25           invention without departing from the scope or spirit of the invention. For example, in the

embodiments mentioned above, various changes may be made to the molecules without departing from the scope and spirit of the invention. For example, tetrahedral shaped core molecules may include carbon, silicon, adamantane, germane, plumlane, or stannane structures or elements. Further, it may be appropriate to make additional modifications or changes to the structures without departing from the scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of the invention provided they come within the scope of the appended claims and their equivalents.

The following articles are incorporated by reference: Joswick, M.D., Campbell, I.H., Brashkov, N.N., Ferraris, J.P. *J. Appl. Phys.* 1996, 80, 2883-2890; Forrest, S.R. *Chem. Rev.* 1997, 97, 1793-1896; Naito, K., Miura, A. *J. Phys. Chem.* 1993, 97, 6240-6248; Naito, K. *Chem. Mater.* 1994, 6, 2343-2350; Tokito, S., Tanaka, H., Okada, A., Taga, Y. *Appl. Phys. Lett.* 1996, 69, 878-880; Tokito, S., Tanaka, H., Noda, K., Okada, A., Taga, Y. *Appl. Phys. Lett.* 1997, 70, 1929-1931; Han, E., Do, L., Niidome, Y., Fujihira, M. *Chem. Lett.* 1994, 969-972.; Fenter, P., Schreiber, F., Bulovic, V., Forrest, S.R. *Chem. Phys. Lett.* 1997, 277, 521-526; Shirota, Y., Kobata, T., Noma, N. *Chem. Lett.* 1989, 1145-1148; Ishikawa, W., Inada, H., Nakano, Y., Shirota, Y. *Chem. Lett.* 1991, 1731-1734; Inada, H., Shirota, Y. *J. Mater. Chem.* 1993, 3, 219-320; Kuwabara, Y., Ogawa, H., Inada, H., Noma, N., Shirota, Y. *Adv. Mater.* 1994, 6, 677; Kageyama, H., Itano, K., Ishikawa, W., Shirota, Y. *J. Mater. Chem.* 1996, 6, 675-676; Tanaka, H., Tokito, S., Taga, Y., Okada, A. *J. Chem. Soc., Chem. Commun.* 1996, 2175-2176; Wilson, L.M., Griffin, A.C. *J. Mater. Chem.* 1993, 3, 991-994; Su, D., Menger, F.M. *Tetrahedron Lett.* 1997, 38, 1485-1487; Liu, F.-Q., Tilley, T.D. 1997, 36, 5090-5096; Mathias, L.J., Reichert, V.R., Muir, A.V.G. *Chem. Mater.* 1993, 5, 4-5; Hartwig, J.F. *Synlett* 1997, 4, 329-340; Louie, J., Driver, M.S., Hamann, B.C., Hartwig, J.F. *J. Org. Chem.* 1997, 62, 1268-1273; Driver, M.S., Hartwig, J.F. *J. Am. Chem. Soc.* 1996, 118, 7217-7218; Marcoux, J.F., Waagaw, S., Buchwald, S.L. *J. Org. Chem.* 1997, 62, 1568-1569; Wolfe, J.P., Wagaw, S., Buchwald, S.L. *J. Am. Chem.*

*Soc.* 1996, *118*, 7215-7216; Louie, J. : Hartwig, J.F., Fry, A.J. *J. Am. Chem. Soc.* 1997, *119*, 11695-11696; Thayumanavan, S., Barlow, S., Marder, S.R. *Chem. Mater.* 1997, *9*, 3231-3235; Oldham, W.J., Jr., Lachicotte, R.J., Bazan, G.C. *J. Am. Chem. Soc.* 1998, *120*, (in press); Itano, K., Ogawa, H., Shirota, Y. *Appl. Phys. Lett.* 1998, *72*, 636-638.

I claim:

1. An organic light emitting device comprising a first electrode, a second electrode, and an organic stack interposed between said first electrode and said second electrode, wherein said organic stack further comprises at least one organic layer, wherein said at least one organic layer further comprises organic compounds such that the organic light emitting device continues to function in temperatures in excess of 145° C.
2. The organic light emitting device of Claim 1, wherein said at least one organic layer comprises organic compounds with tetrahedral shaped core structures.
3. The organic light emitting device of Claim 1, wherein said at least one organic layer comprises organic compounds with tetrahedral shaped core structures containing aromatic side groups.
4. The organic light emitting device of Claim 1, wherein said at least one organic layer comprises organic compounds with tetrahedral shaped core structures containing aromatic amine side groups.
5. The organic light emitting device of Claim 1, wherein said at least one organic layer comprises organic compounds with symmetrical tetrahedral shaped core structures.
6. The organic light emitting device of Claim 1, wherein said at least one organic layer comprises organic compounds with symmetrical tetrahedral shaped core structures containing aromatic side groups.
7. The organic light emitting device of Claim 1, wherein said at least one organic layer comprises organic compounds with symmetrical tetrahedral shaped core structures containing aromatic amine side groups.
8. The organic light emitting device of Claim 3, wherein said aromatic side groups are selected from the group consisting of: phenyl, and substituted analogs thereof.

9. The organic light emitting device of Claim 3, wherein said aromatic side groups are selected from the group consisting of: phenyl, naphthyl, anthracyl, and carbazole.
10. The organic light emitting device of Claim 2, wherein said tetrahedral shaped core structure is a tetraphenyl compound.
11. The organic light emitting device of Claim 10, wherein said tetraphenyl compound is selected from the group consisting of: tetraphenylmethane, tetraphenylsilane, and tetraphenyladamantane.
12. The organic light emitting device of Claim 10, wherein said tetraphenyl compound contains aromatic side groups.
13. The organic light emitting device of Claim 10, wherein said tetraphenyl compound contains aromatic amine side groups.
14. The organic light emitting device of Claim 10, wherein said tetraphenyl compound is functionalized at the *para*-position.
15. The organic light emitting device of Claim 2, wherein said tetrahedral shaped core structures are selected from the group consisting of: tetraphenylmethane, tetraphenylsilane, and tetraphenyladamantane; and wherein said tetrahedral shaped core structures contain aromatic side groups selected from the group consisting of: phenyl, naphthyl, anthracyl, carbazole, and substituted analogs thereof.
16. An organic light emitting device comprising a first electrode, a second electrode, and an organic stack interposed between said first electrode and said second electrode, wherein said organic stack further comprises at least one organic layer, wherein said at least one organic layer further comprises organic compounds with tetrahedral shaped core structures.
17. The organic light emitting device of Claim 16, wherein said at least one organic layer comprises organic compounds with tetrahedral shaped core structures containing aromatic side groups.

18. The organic light emitting device of Claim 16, wherein said at least one organic layer comprises organic compounds with tetrahedral shaped core structures containing aromatic amine side groups.

19. The organic light emitting device of Claim 16, wherein said at least one organic layer comprises organic compounds with symmetrical tetrahedral shaped core structures.

20. The organic light emitting device of Claim 16, wherein said at least one organic layer comprises organic compounds with symmetrical tetrahedral shaped core structures containing aromatic side groups.

21. The organic light emitting device of Claim 16, wherein said at least one organic layer comprises organic compounds with symmetrical tetrahedral shaped core structures containing aromatic amine side groups.

22. The organic light emitting device of Claim 17, wherein said aromatic side groups are selected from the group consisting of: phenyl, and substituted analogs thereof.

23. The organic light emitting device of Claim 17, wherein said aromatic side groups are selected from the group consisting of: phenyl, naphthyl, anthracyl, and carbazole.

24. The organic light emitting device of Claim 16, wherein said tetrahedral shaped core structure is a tetraphenyl compound.

25. The organic light emitting device of Claim 24, wherein said tetraphenyl compound is selected from the group consisting of: tetraphenylmethane, tetraphenylsilane, and tetraphenyladamantane.

26. The organic light emitting device of Claim 24, wherein said tetraphenyl compound contains aromatic side groups.

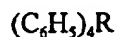
27. The organic light emitting device of Claim 24, wherein said tetraphenyl compound contains aromatic amine side groups.



28. The organic light emitting device of Claim 24, wherein said tetraphenyl compound is functionalized at the *para*-position.

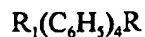
29. The organic light emitting device of Claim 16, wherein said tetrahedral shaped core structures are selected from the group consisting of: tetraphenylmethane, tetraphenylsilane, and tetraphenyladamantane; and wherein said tetrahedral shaped core structures contain aromatic side groups selected from the group consisting of: phenyl, naphthyl, anthracyl, carbazole, and substituted analogs thereof.

30. An organic light emitting device comprising a first electrode, a second electrode, and an organic stack interposed between said first electrode and said second electrode, wherein said organic stack further comprises at least one organic layer, wherein said at least one organic layer further comprises organic compounds with tetrahedral shaped core structures, wherein said tetrahedral shaped core structures satisfy one or more of the formula:



wherein R is selected from the group consisting of: C, Si, adamantane ( $\text{C}_{10}\text{H}_{12}$ ), Ge, Pb, or Sn.

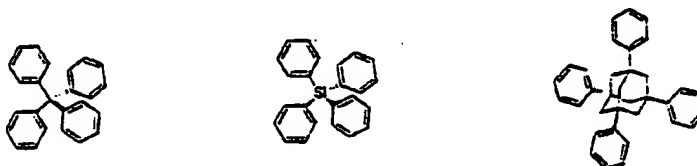
31. An organic light emitting device comprising a first electrode, a second electrode, and an organic stack interposed between said first electrode and said second electrode, wherein said organic stack further comprises at least one organic layer, wherein said at least one organic layer further comprises organic compounds with tetrahedral shaped core structures, wherein said organic compounds satisfy one or more of the formula:



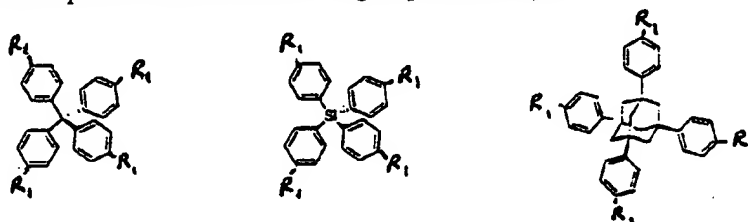
wherein R1 is selected from the group consisting of: aromatic groups and aromatic amine groups, and

wherein R is selected from the group consisting of: C, Si, adamantane ( $\text{C}_{10}\text{H}_{12}$ ), Ge, Pb, or Sn.

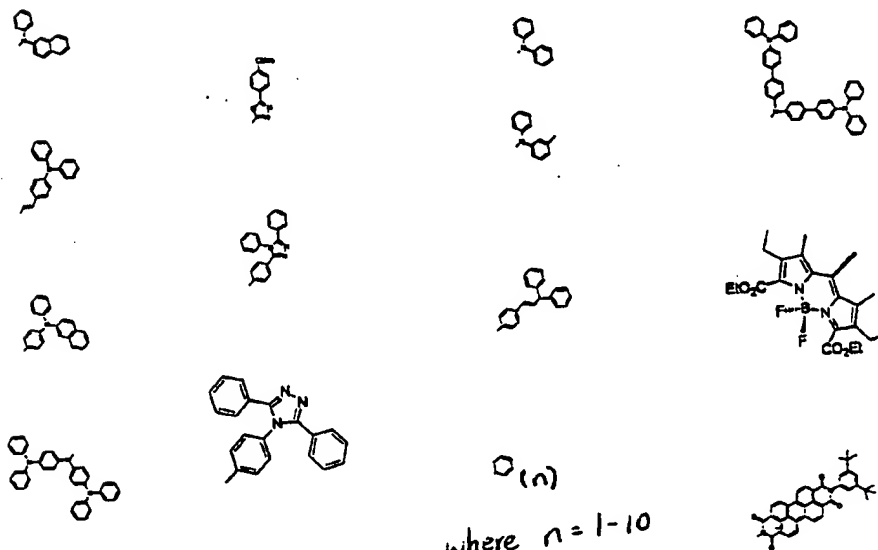
32. An organic light emitting device comprising a first electrode, a second electrode, and an organic stack interposed between said first electrode and said second electrode, wherein said organic stack further comprises at least one organic layer, said at least one organic layer further comprising organic compounds with tetrahedral shaped core structures selected from the group consisting of:



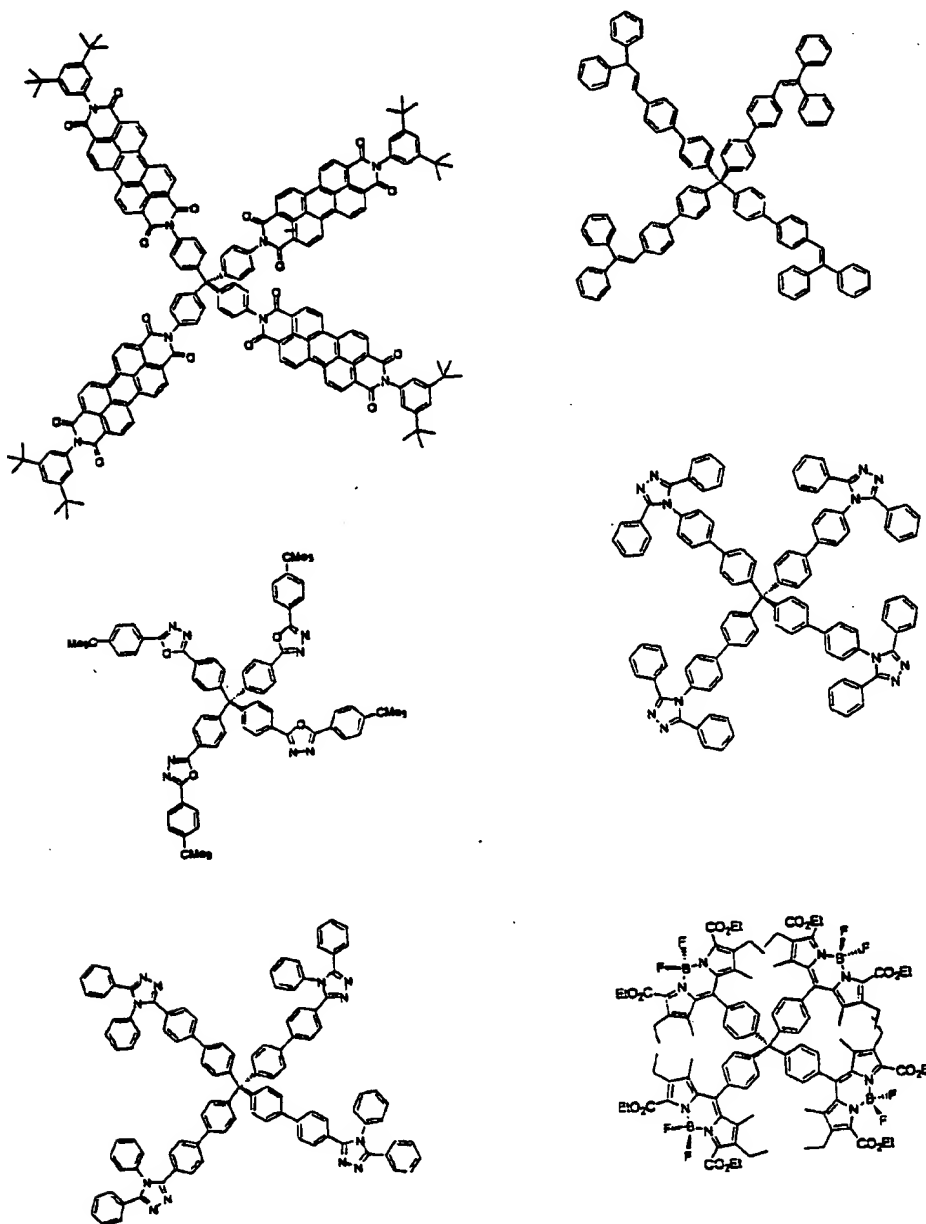
33. An organic light emitting device comprising a first electrode, a second electrode, and an organic stack interposed between said first electrode and said second electrode, wherein said organic stack further comprises at least one organic layer, said at least one organic layer further comprising organic compounds selected from the group consisting of:

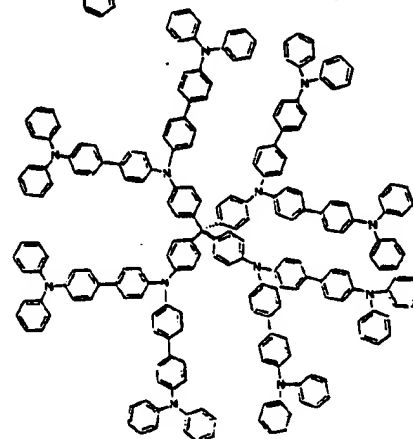
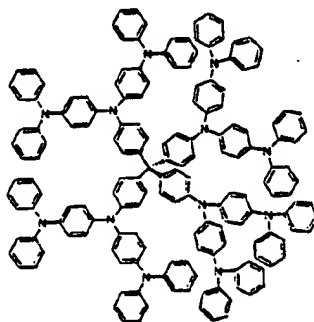
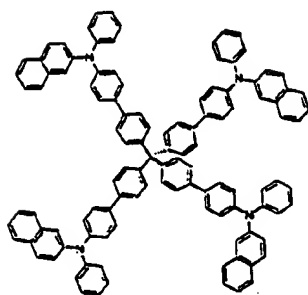
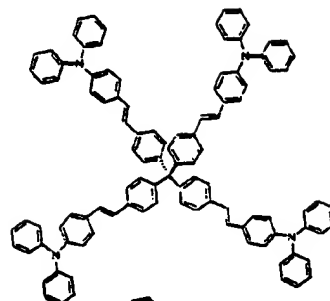
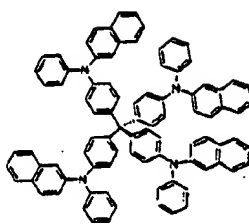
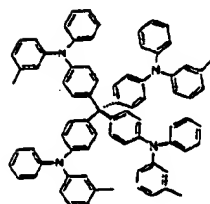
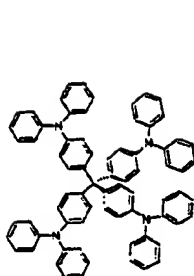
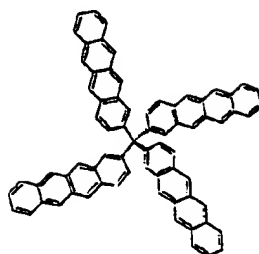
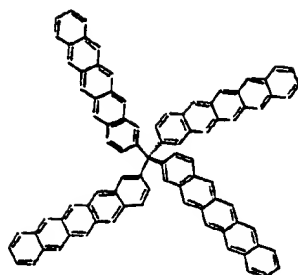
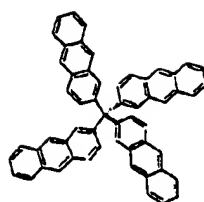
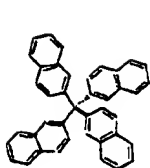


wherein R1 is selected from the group consisting of:



34. An organic light emitting device comprising a first electrode, a second electrode, and an organic stack interposed between said first electrode and said second electrode, said organic stack further comprising at least one organic layer, said at least one organic layer further comprising organic compounds with a tetraphenyl core selected from the group consisting of:





35. The organic light emitting device of Claim 34, wherein said tetraphenyl core is selected from the group consisting of: tetraphenylmethane, tetraphenylsilane, and tetraphenyladamantane.

36. An organic light emitting device having a first electrode, a second electrode, and an organic stack interposed between said first electrode and said second electrode, wherein said organic stack further comprises at least one hole transport layer, said at least one hole transport layer further comprises organic compounds with tetrahedral shaped core structures.

37. The organic light emitting device of Claim 36, wherein said at least one hole transport layer includes organic compounds with tetrahedral shaped structures containing aromatic side groups.

38. The organic light emitting device of Claim 36, wherein said at least one hole transport layer includes organic compounds with tetrahedral shaped structures containing aromatic amine side groups.

39. The organic light emitting device of Claim 36, wherein said at least one hole transport layer includes organic compounds with symmetrical tetrahedral shaped core structures.

40. The organic light emitting device of Claim 36, wherein said at least one hole transport layer includes organic compounds with symmetrical tetrahedral shaped core structures containing aromatic side groups.

41. The organic light emitting device of Claim 36, wherein said at least one hole transport layer includes organic compounds with symmetrical tetrahedral shaped core structures containing aromatic amine side groups.

42. The organic light emitting device of Claim 37, wherein said aromatic side groups are selected from the group consisting of: phenyl, and substituted analogs thereof.

43. The organic light emitting device of Claim 37, wherein said aromatic side groups are selected from the group consisting of: phenyl, naphthyl, anthracyl, and carbazole.

44. The organic light emitting device of Claim 36, wherein said tetrahedral shaped core structure is a tetraphenyl compound.

45. The organic light emitting device of Claim 44, wherein said tetraphenyl compound is selected from the group consisting of: tetraphenylmethane, tetraphenylsilane, and tetraphenyladamantane.

46. The organic light emitting device of Claim 44, wherein said tetraphenyl compound contains aromatic side groups.

47. The organic light emitting device of Claim 44, wherein said tetraphenyl compound contains aromatic amine side groups.

48. The organic light emitting device of Claim 44, wherein said tetraphenyl compound is functionalized at the *para*-position.

49. The organic light emitting device of Claim 36, wherein said tetrahedral shaped core structures are selected from the group consisting of: tetraphenylmethane, tetraphenylsilane, and tetraphenyladamantane; and wherein said tetrahedral shaped core structures contain aromatic side groups selected from the group consisting of: phenyl, naphthyl, anthracyl, carbazole, and substituted analogs thereof.

50. An organic light emitting device having a first electrode, a second electrode, and an organic stack interposed between said first electrode and said second electrode, wherein said organic stack further comprises at least one organic layer, said organic layer further comprising organic compounds containing tetrahedral shaped core structures selected from the group consisting of: silicon based tetrahedral core structures, carbon based tetrahedral core structures, and adamantane based tetrahedral core structures.

51. The organic light emitting device of Claim 50, wherein said tetrahedral shaped core structures contain aromatic side groups.

52. The organic light emitting device of Claim 50, wherein said tetrahedral shaped core structures contain aromatic amine side groups.

53. The organic light emitting device of Claim 51, wherein said aromatic side groups are selected from the group consisting of: phenyl, and substituted analogs thereof.

54. The organic light emitting device of Claim 51, wherein said aromatic side groups are selected from the group consisting of: phenyl, naphthyl, anthracyl, and carbazole.

55. The organic light emitting device of Claim 2, wherein said tetrahedral shaped core structures contain aromatic side groups oriented away from one another at angles between  $100^{\circ}$  and  $120^{\circ}$ .

56. The organic light emitting device of Claim 2, wherein said tetrahedral shaped core structures contain aromatic amine side groups oriented away from one another at angles between  $100^{\circ}$  and  $120^{\circ}$ .

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/15437

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
IPC(6) :H05B 33/00 US CL :428/690		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
U.S. : 428/690, 691, 917; 313/503, 504, 506		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,716,722 A [HAMADA et al.] 10 February 1998, see entire document.	1-56
A	US 5,077,142 A [SAKON et al.] 31 December 1991, see entire document.	1-56
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *G* document member of the same patent family	
*A* document defining the general state of the art which is not considered to be of particular relevance		
*E* earlier document published on or after the international filing date		
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)		
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search	Date of mailing of the international search report	
19 OCTOBER 1999	03 NOV 1999	
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer CHARLES R. NOLD <i>Charles R. Nold</i> Telephone No. (703) 308-2351	

Form PCT/ISA/210 (second sheet)(July 1992)\*

04/30/2003, EAST Version: 1.03.0002